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## SYNTHESIS OF WEAR-RESISTANT CERAMICS

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The intensity of the stimulating effect of Cr, Mn, and Fe oxides on the processes of pyroxene formation of glass ceramics is established. The possibility of synthesis of glass ceramics based on compositions containing less than 50% SiO<sub>2</sub> is confirmed.

Glass ceramics have a special place among the wide class of inorganic materials with respect to their compositions and application areas. Wear-resistant glass ceramics are based on crystalline phases, primarily of the pyroxene series, including solid solutions based on diopside MgO · CaO · 2SiO<sub>2</sub> capable of incorporating substantial quantities of additional oxides (Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, etc.) in its crystalline lattice and provide for the formation of a monomineral phase in crystallization.

The propensity of diopside for wide isomorphism allows easy incorporation of various cations into its crystal lattice. Within the MgO–CaO–SiO<sub>2</sub> system, compositions which, in cooling of the melt, produce diopside as the main phase are found within the following limits (wt.%): 55–70 SiO<sub>2</sub>, 5–35 CaO, 10–30 MgO. Pyroxene-formation processes based on these ratios have been thoroughly investigated and analyzed in [1].

Glasses used to produce pyroxene glass ceramics with fluorine as the crystallization catalyst have the following composition (wt.%): 66–70 SiO<sub>2</sub>, 15–26 CaO, 8–15 MgO and also 5–7% of Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O each, and 5% Fe<sub>2</sub>O<sub>3</sub> [2].

It is known that TiO<sub>2</sub> is not effective as a crystallization catalyst for glasses of the “diopside” system. Cr<sub>2</sub>O<sub>3</sub> and CaF<sub>2</sub> actively facilitate the formation of pyroxene.

Pyroxene glass ceramics can be easily synthesized on the basis of mineral rocks. In particular, basalt-based petroglass ceramics have better parameters than industrially produced basalt-based stone casting. They have lower porosity, a finer-grained structure, and increased mechanical strength, and they are also more resistant to the effect of acids and alkalis [2]. The substantial increase in the strength of material in transition from melted basalt to petroglass ceramic is due to the finer-grained structure of petroglass ceramics (the stresses at crystal boundaries decrease). Furthermore, petroglass ceramic crystals with their small dimensions (up to 1 μm) contain fewer defects than large stone-cast crystals

(50 μm). An increase in the strength of petroglass ceramics is also facilitated by a smaller difference in the TCLEs of the crystalline phases and the residual vitreous phase. This reduces the internal stresses in the material.

As the main material for the synthesis of pyroxene petroglass ceramics was natural diabase from Belarus containing from 45 to 52 wt.% SiO<sub>2</sub>, the pyroxene-formation processes had to be studied in the lower-silica range of the “diopside” system, i.e., for the content of SiO<sub>2</sub> ranging from 40 to 55 mol.%. Model glasses synthesized for this purpose were based on the low-silica range of the system with small quantities of technological additives (5 mol.% Na<sub>2</sub>O and 5 mol.% Al<sub>2</sub>O<sub>3</sub>) that did not contain crystallization catalysts, whereas other glasses contained oxides of 3d-elements (Cr<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>) acting as crystallization catalysts.

The d-elements of period IV are built of M-layers up to 18 electrons. Based on the type of filling d-orbitals, Cr and Mn belong to the subfamily of scandium, and Fe belongs to the subfamily of iron [3].

The stable degree of oxidation for chromium are III and IV. Chromium is amphoteric like other d-elements and has both cation and anion complexes. As the degree of oxidation grows, the stability of the anion complexes increases and that of the cation complexes decreases. Manganese has typical oxidation degrees II, IV, and VIII. As the degree of oxidation grows, the tendency for the formation of anion complexes increases. Iron has typical degrees of oxidation II and III. Bivalent iron has typical coordination number 6 and has both cation and anion complexes. The coordination number of Fe(III) is equal to six and four.

Considering different types of hybridization, one can assume unequal behavior of Cr, Mn, and Fe oxides in glasses and, accordingly, different participation in the phase transformations in crystallization. The effect of the oxides of the specified 3d-elements on the crystallization processes was repeatedly studied in pyroxene glasses, including glasses based on slag, and most frequently as combinations of the above elements [1].

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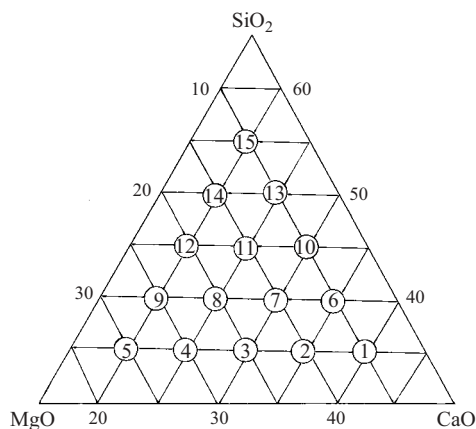


Fig. 1. Glass compositions in the model system (molar content).

The composition of model glass systems (M-systems), i.e., glasses without crystallization catalysts, varied in the following limits (mol.%): 40–55  $\text{SiO}_2$ , 20–40  $\text{CaO}$ , 10–30  $\text{MgO}$  with a constant molar content of 5%  $\text{Na}_2\text{O}$  and 5%  $\text{Al}_2\text{O}_3$  (Fig. 1). Besides, the following additives were introduced into glasses of this system above 100%: 1, 2, and 3 wt.%  $\text{Cr}_2\text{O}_3$  (Cr system); 3, 6, and 9 wt.%  $\text{Mn}_2\text{O}_3$  (Mn system), and 3, 6, and 9 wt.%  $\text{Fe}_2\text{O}_3$  (Fe system).

The glasses were melted in a gas furnace at 1430–1450°C with a 1-h exposure. All glasses were well melted and clarified, except for the glasses with 2 and 3%  $\text{Cr}_2\text{O}_3$ , which crystallized in molding.

Analyzing the results of gradient crystallization within the temperature range of 600–1000°C, it was found that glasses of the M-system crystallize in the range of 800–950°C and form a loose large-crystal structure or a surface crystalline crust. The main crystalline phase is a solid solution of diopside.

In the Cr system with 1%  $\text{Cr}_2\text{O}_3$ , a volume glass-ceramic structure is formed only with an increased content of  $\text{MgO}$  (25–30%) and 40–45 mol.% of  $\text{SiO}_2$ ; i.e., compositions 4, 5, 9, and 12 (Fig. 1). In adding 2%  $\text{Cr}_2\text{O}_3$ , the amount of glasses with a glass-ceramic structure significantly increases, and with 3%  $\text{Cr}_2\text{O}_3$ , all glasses form a glass-ceramic structure.

In contrast to the active effect of  $\text{Cr}_2\text{O}_3$  on the crystallization processes in experimental glasses, the introduction of  $\text{Mn}_2\text{O}_3$  does not have this effect. The glasses do not undergo volume crystallization; on the contrary, when 3%  $\text{Mn}_2\text{O}_3$  is added, the glass only becomes coated with a thin film but remains transparent. With 6 and 9% of  $\text{Mn}_2\text{O}_3$ , a surface crystalline crust emerges on the glasses under heat treatment. No glass-ceramic structure was registered in samples of the considered glass compositions.

Introduction of 3%  $\text{Fe}_2\text{O}_3$  does not ensure volume crystallization, and only a crystalline film or a crust is formed. However, on further increasing the  $\text{Fe}_2\text{O}_3$  content to 6%, glasses 4, 5, and 9 form a glass-ceramic structure, and with 9%  $\text{Fe}_2\text{O}_3$ , the range of glass-ceramic-forming compositions expands to include compositions 3, 8, and 12 (Fig. 1).

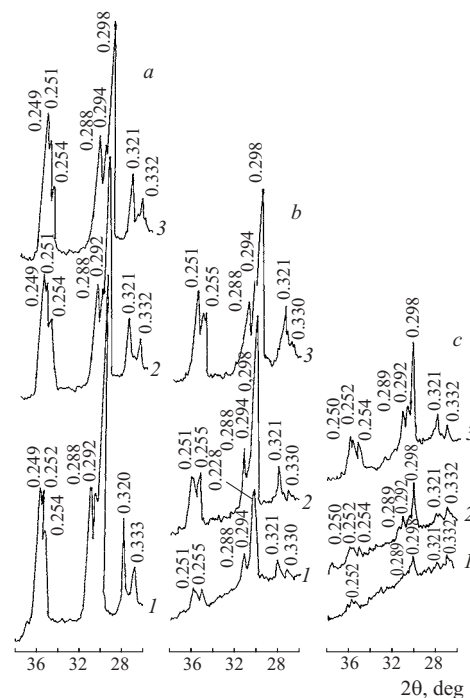


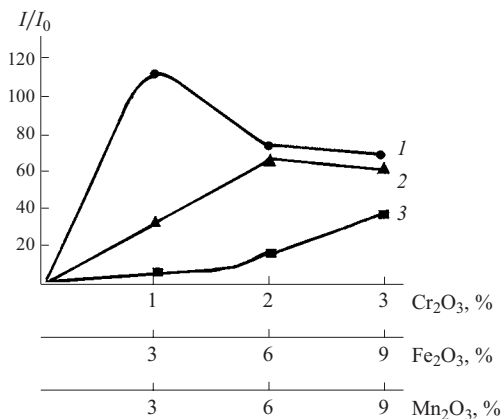
Fig. 2. X-ray patterns of glass 12 crystallized at 900°C with different contents of 3d-element oxides: a) glass of Cr system [1, 2, and 3) 1, 2, and 3 %  $\text{Cr}_2\text{O}_3$ ]; b) glass of Fe system [1, 2, and 3) 3, 6, and 9%  $\text{Fe}_2\text{O}_3$ ]; c) glass of Mn system [1, 2, and 3) 3, 6, and 9%  $\text{Mn}_2\text{O}_3$ ].

Figure 2 shows the x-ray patterns of glass 12 with different contents of 3d-element oxides after heat treatment at 900°C. It is interesting that the main crystalline phase in all cases is a diopside-based solid solution, i.e., a pyroxene crystalline phase capable of ensuring high wear resistance.

The diffraction maxima and their characteristics (doublets and triplets) confirm the formation of a diopside-like solid solution of the type of  $\text{Ca}(\text{Mg}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6$ . When  $\text{Fe}_2\text{O}_3$  is used, a pyroxene solid solution of the type of  $\text{Ca}(\text{Mg}, \text{Fe}^{3+}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6$  is formed.

The introduction of 1%  $\text{Cr}_2\text{O}_3$  contributes most actively to the formation of the maximum amount of the pyroxene phase. On further increasing the  $\text{Cr}_2\text{O}_3$  content in glass, the amount of pyroxene phase in the crystallization products starts decreasing. This is apparently due to the fact that an excessive content of  $\text{Cr}_2\text{O}_3$  results in active formation of  $\text{Cr}_2\text{O}_3$  crystals or chromium-magnesium spinellide, which does not promote nucleation of a great number of crystallization centers of the main pyroxene phase.

The active role of  $\text{Fe}_2\text{O}_3$  is well manifested only after introducing it in the amount of 6% or more; however, a coarse-crystalline, partly porous structure is formed in this case. The above regularities are substantiated by a modification of the relative intensity of the main diffraction maximum of the solid solution of diopside ( $d = 0.298$  nm) on the diffraction patterns (Figs. 2 and 3).



**Fig. 3.** Variations in relative intensity of the main diopside maximum (0.289 nm) on x-ray patterns of crystallized glasses containing  $\text{Cr}_2\text{O}_3$  (1),  $\text{Fe}_2\text{O}_3$  (2), or  $\text{Mn}_2\text{O}_3$  (3).

Thus, in studying the mechanism of formation of a fine-crystalline volume structure in heat treatment of the considered glasses, a sharp distinction in nucleation and growth of crystals was revealed upon the introduction of the specified oxides.

Thus,  $\text{Mn}_2\text{O}_3$  in the amount of 3, 6, and 9% does not activate pyroxene formation, does not facilitate the formation of a volume glass-ceramic structure, but acts as a normal modifying oxide in glass.

$\text{Fe}_2\text{O}_3$ , which is also introduced in the amount of 3, 6, and 9%, facilitates volume crystallization with the formation of the pyroxene phase, but only in a limited composition range. The data of electron-microscope studies indicate that nucleation of crystallization centers in this case at the first

stage proceeds by way of formation of two non-mixing liquid phases, one of which is rich in oxides ( $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Fe}_2\text{O}_3$  or  $\text{FeO}$ ) and the second has a high silica content.

In contrast,  $\text{Cr}_2\text{O}_3$  is an active stimulator of crystallization of the pyroxene phase of the type of  $\text{Ca}(\text{Mg}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6$ . The pyroxene formation in this case proceeds at first by way of nucleation of chromium-spinellides (they are registered in the form of rare crystals of cubic syngony only by using an electron microscope), and then the pyroxene solid solution is actively formed.

Consequently, the differences in types and structures of  $\text{Cr}^{3+}$ ,  $\text{Mn}^{3+}$ , and  $\text{Fe}^{3+}$  atoms determine as well the differences in stimulating the crystallization of the considered glasses, and the intensity of the characteristic maxima of diopside (0.298, 0.292, 0.289, and 0.252 nm) decreases in the sequence of  $\text{Cr}_2\text{O}_3 \rightarrow \text{Fe}_2\text{O}_3 \rightarrow \text{Mn}_2\text{O}_3$ .

The results of the studies confirm the possibility of synthesis of glass ceramics with the main pyroxene phase, i.e., a solid solution of the diopside type based on compositions containing less than 50%  $\text{SiO}_2$ , i.e., virtually coinciding with the composition of natural metadiabase, under stimulation of the crystallization processes using chromium oxides.

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